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HEAT ACCUMULATING MEDIUM
[Wärmespeichermedium]

Günter Hildebrand, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
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Description /1*

First, the invention relates to a heat accumulating medium, such as paraffin, which solidifies while crystal structures form, for latent heat accumulators or latent cold accumulators.

As is known to the art, latent heat accumulators are of service in the efficiency-enhancing temporal decoupling of the generation of heat or cold and the subsequent consumption of heat or cold. Decoupling facilitates long, continuous running times of heat and cold generators with high efficiencies and low start-up, running, and stoppage costs. They are, for instance, used in facilities for the generation of heat from solar energy or from fossil energy carriers, but, in addition, they are also used in cooling cycles.

With regard to the state of the art, reference is made to DE-A1 2741829, for instance. From this document, the use of amounts of paraffin enclosed in a plastic shell as a heat accumulating medium in a latent heat accumulator is known to the art. The plastic shells, in turn, are located inside an accumulator container which is filled with water. In these kinds of latent heat accumulators, the transport of heat merely takes place via heat conduction through the plastic shell to the paraffin. These kinds of accumulators are referred to as static accumulators.

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*Number in the margin indicates column in the foreign text.

Moreover, so-called dynamic latent heat accumulators are known to the art in which reference is made to DD 236862 and DD 280113, for instance. Furthermore, with respect to the state of the art, reference is made to DE-A1 4122859 in this context. In this regard, it is viewed as disadvantageous that the heat accumulating medium, such as paraffin, can only be penetrated by the heat transfer medium, perhaps, evaporating water or an alcohol-based liquid, with difficulty. As a result, delays in the response of the latent heat accumulator are registered when heat is supplied.

On the basis of the most recent state of the art represented, it is an objective of the invention to provide a heat accumulating medium, such as paraffin, for a latent heat accumulator (latent cold accumulator) which, specifically, will lead to an improved response behavior when heat is supplied. Another consideration is to be that the requirements of environmental tolerableness of the heat accumulating medium are met.

This objective is realized in the subject of Claim 1, whereas this entails that the crystal structure is modified by a structural additive, preferably, in the sense of hollow structures, such as, for instance, hollow cones. The platelet form of the crystals which is known to the art for a paraffin-based heat accumulating medium accordingly changes into hollow cone-shaped or tubular crystal structures. In accordance with the invention, it has been recognized

that, through a direct modification of the crystal structures of the heat accumulating medium, such as, particularly, paraffin, it is possible to determinatively improve the response behavior of the heat accumulating medium when heat is supplied. Surprisingly, it has become evident that, through such a crystal modification, the assumption of an equally porous structure by the heat accumulating medium, such as paraffin, can be achieved. Water vapors forming when heat is supplied not only penetrate into the lower area of the heat accumulating medium, but also very rapidly intersperse the entire heat accumulating medium. Thus, the result is an abrupt response, i.e., a melt-down of the heat accumulating medium, and, thus, the accumulation of heat. To the extent that paraffin is mentioned in the above text /2 and the following text, it is to be interpreted as paraffinic hydrocarbons, such as n-paraffins (liquid) macroparaffins, intermediate paraffins, and micocrystalline waxes. On an individual basis, these also comprise so-called intermediate paraffins and microcrystalline waxes. An advancement of the invention provides that the structural additive be homogeneously dissolved in the heat accumulating medium. On an individual basis, structural additives on the basis of polyalkyl methacrylates (PAMA) and polyalkyl acrylates (PAA) have proved to be successful individually or in combinations, specifically. Their crystal-modifying effect is caused by the incorporation of the polymer molecules into the growing paraffin

crystals and because the further growth of this crystal form is prevented. Due to the presence of polymer molecules in paraffin, even in an associated form in the homogenous solution in paraffin, paraffins can overgrow on the specific associate. Hollow cones are formed which are no longer capable of forming networks. Due to the synergistic effect of these structural additives on the crystallization behavior of the paraffins, a formation of hollow spaces and, therefore, an improvement of the permeability of the heat accumulating medium paraffin (for instance, for water vapors) is realized in comparison with paraffins that have not been compounded in this way. In general, ethylene vinyl acetate copolymers (EVA), ethylene propylene copolymers (OCP), diene styrene copolymers, are suitable as structural additives both as single components and in a mixture, as well as alkylated naphthalene (paraflow). The percentage of structural additives starts at a wt.% fraction, realistically, at about 0.01 wt.% and demonstrates perceivable changes in the sense of an improvement up to a percentage of about 1 wt.%, specifically. A higher dosage may prove to be disadvantageous because a great number of small crystallites are formed which results in a dense crystal packing and, thus, adversely affects the permeability of the heat accumulating medium. Individually, the percentage of structural additives also depends on the melting temperature of the heat accumulating medium. As a rule, with a higher-melting heat

accumulating medium or higher-melting paraffins, a higher weight percentage of structural additives is required to achieve the same success than with a lower-melting heat accumulating medium. A further advancement of the invention provides that, in the case of solid, paraffinic hydrocarbons (macroparaffins, intermediate paraffins, microcrystalline waxes), the heat accumulating medium contains liquid components (low-melting n- and isoalkanes, as well as naphthene), as well as a so-called oil constituent. As is known to the art, solid, paraffinic hydrocarbons are obtained from vacuum distillate fractions by means of various technological separation steps which require a certain oil percentage. With regard to the use of a heat accumulating medium of the type described in greater depth here, it has proved advantageous if the oil percentage is standardized to between 0.1 and 10 wt.%. If the heat accumulating medium is supplied with heat in a solidified state in this configuration, the resulting effect is that oil constituents which are incorporated in an even distribution are equally exudated by the heat accumulating medium and run off in downward direction - as they follow gravity. Thereby, paths are created in the heat accumulating medium which are increased in size in comparison to the mentioned "porosity" which further promotes a rapid penetration by the heat transfer medium. Aside from that, such an /3
oil constituent in the heat accumulating medium is useful only if the heat accumulating medium is solidified at room temperature. Moreover,

it is preferable within the framework of the invention that the carbon chain lengths are selectively standardized in the paraffin, i.e., that a specific cut is provided which is selected in such a way that it is comparatively narrow. A narrow cut means that only chain lengths of a few numbers are included. For instance, C14 to C16, or C20 to C23. Because, at least, on an industrial scale, the cut always changes in the sense of a frequency distribution, if no special precautionary measures are taken, the above-explained measure means that, at least, the by far greatest majority of any given quantity of the heat accumulating medium is formed by the chain lengths which encompass these few numbers. In detail, the cut is devised according to the desired melting temperature. Moreover, it has proved to be especially advantageous to prefer the even-numbered, regular C chains (n-alkanes). These exhibit a surprisingly great heat accumulating capacity during phase changes in the mentioned insulation. In this process, consideration should, in the same manner, be paid to the fact that, at least, on an industrial scale, it is not, or not always, possible to produce these C chains "purely" in the sense of even-numbering at justifiable cost. In any event, it is advantageous to enrich them to the extent possible. An additional preferred configuration of the invention provides that boiling structures or nucleators exhibit such a specific weight that they, at least, float in the heat accumulating medium. Because, depending upon the

liquefied or solidified state, the heat accumulating medium may exhibit various specific weights, it is especially preferred that these boiling structures or nucleators be adapted to the specific weight in the liquefied state. If they are homogeneously distributed there, no demixing results, even if various specific weights are present. This specific weight can, for instance, be achieved by means of plastic particles or sandiver particles. Furthermore, the boiling structures or nucleators, preferably, are relatively small in the millimeter and millimeter fraction range, so that they can be present in the heat accumulating medium in extremely fine dispersion. Especially in combination with the above-mentioned measure, the modification of the crystal structure of the heat accumulating medium in the sense of hollow structures by means of a structure-forming agent, these corpuscles not only prove to be advantageous in the sense of nucleators during the condensation process, but also during boiling in the heat accumulating medium. As it were, the porously standardized structure of the heat accumulating medium is permeated by water vapors when heat is supplied if water is used as the heat transfer medium, for instance, which immediately recondensates on the cooler heat accumulating medium. Successively applied vapors, in turn, result in boiling processes which, then, (again) immediately begin in an intensified fashion in the heat accumulating medium in virtually uniform fashion due to the corpuscles which are also

arranged dispersed in the heat accumulating medium. The characterization that the boiling structures or nucleators are, at least, configured so that they float in the heat accumulating medium (due to their specific weight) means that additional corpuscles (an /4
additional group of these) may be provided which are also configured, so that they float in the heat transfer medium. This, especially, is the case if the heat transfer medium is a medium which is lower in specific weight in relation to the heat accumulating medium, such as, for instance, alcohol. Regardless of this, it is preferable within the framework of the invention that the heat transfer medium also contains boiling structures or nucleators (which, however, as a rule, only exercise the function of a boiling structure in the heat transfer medium). If the heat transfer medium is water, these boiling structures can be of greater specific weight than water and will collect on the bottom of a pertinent latent heat accumulator (because, again, in the preferred dynamic latent heat accumulators, generally, the lighter medium settles over the heavier medium due to the specific weight). One configuration of the corpuscles, even in the heat transfer medium in the sense of a floatation or near floatation, also has advantages to the extent that, if the heat transfer medium is of greater specific weight than the heat accumulating medium, these corpuscles are flung into the heat accumulating medium especially forcefully when the boiling process starts which further accelerates

the desired melting process of the heat accumulating medium. If the functions can be differentiated with regard to a nucleator and with regard to a suppression of a boiling delay, these will, as a rule, after all, be triggered by the same corpuscles, so that, to that extent, no differentiation will be required where materials are concerned. These kinds of corpuscles, preferably, are contained in the heat accumulating medium or the heat transfer medium in a scale of 1 to 10 wt.%. It is self-understood that even vol.% fractions bring about a certain effect. However, the boiling structures or nucleators can also be configured in such a way that, because of their specific weight, they will float partially in the heat transfer medium and partially in the heat accumulating medium. In a practical configuration - if, for instance, the heat transfer medium (water) is specifically heavier than the heat accumulating medium (paraffin) - this can, for instance, be achieved in that the boiling structures or nucleators exhibit a specific weight which lies between the specific weight of the heat accumulating medium and the specific weight of the heat transfer medium. Accordingly then, these corpuscles would arrange themselves on the boundary layer between the two media. This fact can be used to advantage to the extent that these corpuscles are configured with oblong stalk- or tentacle-like appendices with which they then protrude into the heat transfer medium, and that, specifically, they do so to the degree which is necessary to

compensate for their excess weight in relation to the heat accumulating medium. In this process, it is further preferred that the configuration be realized so that only the stalk- or tentacle-like appendices will protrude into the heat transfer medium. Besides that, the nucleators/boiling structures can also be selected in their specific weight, so that they are only located in the heat accumulating medium (floating) or in the heat transfer medium. An additional preferred configuration provides that the filling medium is equipped with an anti-foaming agent. Anti-foaming agents for /5
paraffins or media that are similar to paraffin are basically known to the art. To that extent, reference can be made to literature in that regard. In respect to a filling medium for a latent heat accumulator or latent cold accumulator, such an anti-foaming agent acquires quite substantial significance. A foam formation of the heat accumulating medium results in worse local coefficients of heat transfer on heat-exchanging surfaces and, hence, in reduced heat-transfer efficiency. By adding an anti-foaming agent to the heat accumulating medium, a further improvement can be realized in this respect. Anti-foaming agents known to the art, for instance, include those on the basis of silicones, polyalkoxylates, fatty alcohol alkoxylates, or carboxylic acid esters. A further advancement also provides that the heat accumulating medium exhibits an antioxidant. It obviates an aging process of the heat accumulating medium, for instance, through a

cleavage of the carbon chains. Antioxidants on the basis of multi-alkylated phenols and nitrogen-substituted phenylene diamins are known to the art with respect to paraffins. In this regard, reference is also made to the literature regarding paraffins.

Moreover, the subject of the invention is an additive for a heat accumulating medium, like paraffin, for a latent heat accumulator (latent cold accumulator) which crystallizes by forming crystal structures, which contains structural additives that modify the crystal structures in the sense of hollow structures, such as, for instance, hollow cones. Where details are concerned, reference is made to the above exposition with respect to the structural additive. The additive can be added to existing heat accumulating media, especially those on a paraffin basis, in order to improve their characteristics in the manner which was described in detail above. Moreover, the additive may also contain boiling structures, particularly, those of different specific weights which are appropriate to, on the one hand, be present in the heat accumulating medium in a floating state, while, on the other hand, floating in the heat transfer medium, or settling. Furthermore, the additive may also contain an anti-foaming agent and/or an antioxidant, whereas, again, reference is made to the above description with regard to the details of the previously mentioned components.

Moreover, the subject of the invention is a latent heat accumulator or latent cold accumulator which contains a heat accumulating medium in one of the above-described configurations. However, in this context, yet another configuration is preferred with regard to the boiling structures or nucleators as fixed installations in the latent heat accumulator. Here, the boiling structures or nucleators can particularly be realized by means of planar elements, furthermore, curved planar elements. These planar elements are appropriately provided, so that they will partially protrude into the area of the heat transfer medium and partially into the area of the heat accumulating medium.

Finally, the subject of this application is also the use of paraffin with a certain oil constituent, as described in greater detail above, for use in a heat accumulating medium for a latent heat accumulator.

In the following text, an example of a latent heat accumulator with a heat accumulating medium of the type herein described will be explained by means of the attached drawings. Shown are: /6

Figure 1, a hermetically sealed accumulator container with a magnified representation for the schematic illustration of the shell structures and boiling structures/nucleators in the heat accumulating medium;

Figure 2, a representation in accordance with Fig. 1 with modified boiling structures/nucleators;

Figure 3, a representation in accordance with Fig. 1 or Fig. 2 with fixed installations as boiling structures or nucleators.

Figure 1 depicts a hermetically sealed accumulator container which, in particular, consists of a metallic material, such as, preferably, aluminum. In the condition shown in the drawing, the heat accumulator medium (2) is in a solidified state. It is solidified paraffin. Essentially, pure water (3) is located in the lower area of the latent heat accumulator (1) as a heat transfer medium, while a vacuum air space or vacuum is located in the upper area (4) of the latent heat accumulator (1).

The crystal structure of the heat accumulating medium (2) is - schematically - suggested in the magnified representation. These are structures of a hollow cone-like type which, as a whole, then result in the desired micro "porosity" of the heat accumulator medium (2).

Boiling structures (5) which are arranged in the heat transfer medium (3) ensure a nearly simultaneous boiling of the water (3) when heat is introduced via a heat exchanger which protrudes into the heat transfer medium (3), for instance, or which can simply be obtained by heating the latent heat accumulator (1) on its bottom. Also - additional - boiling structures (5) or nucleators (6) are arranged in the heat accumulating medium (2). Because of their specific weight,

the nucleators (6) even float in the heat accumulating medium (2) if the heat accumulating medium (2) is liquefied.

If heat is supplied to the latent heat accumulator (1) - in the bottom area - the water (3) begins to boil at a certain temperature which is essentially determined by the vacuum pressure in the space (4), and the created water vapors penetrate into the heat accumulating medium (2). Due to a structural additive which is homogeneously distributed in the heat accumulating medium (2), the heat accumulating medium (2) also has a porous character in the solidified state, so that the water vapors can almost explosively supply a large surface and the heat accumulating medium (2), accordingly, suddenly runs through a phase change and liquefies. Thus, the water vapors rapidly penetrate up to the upper area (4) where, usually, a condensation takes place due to a dissipation of heat. The water vapors collect in droplets of water and run back into the bottom area of the latent heat accumulator (1). If more heat is withdrawn from the latent heat accumulator (1) in its head area than what is supplied to its bottom area, the latent heat accumulator (1) discharges and if a drop occurs below a certain temperature, the heat accumulating medium (2), again, runs through a phase change (from liquid to solid), whereafter the state occurs which is shown in the attached drawings.

Figure 2 - essentially in schematic form - depicts boiling /7 structures or nucleators (6') which exhibit stalk- or tentacle-like appendices (7). As a whole, these may be configured somewhat heavier than the actual nucleators (6') - which are represented in globular shape here. As a whole, the specific weight of such a corpuscle is of higher than the weight of the heat accumulating medium (2), but lower than the weight of the heat transfer medium (3), so that the boiling structures or nucleators (6') swim in the heat transfer medium (3) while utilizing the buoyancy. From this explanation, it also becomes clear that the corpuscles (6'), to the extent that they are, for instance, composed of various materials, also possess parts, for instance, the appendices (7), which consist of a material that is also specifically heavier than the heat transfer medium (3).

Furthermore, Fig. 2 shows that, moreover, additional boiling structures (5) or nucleators (6) are present in the latent heat accumulator (1) in the form that has already been described with regard to Fig. 1.

Due to the appendices (7), substantial effects also result with respect to a rapid response of the latent heat accumulator (1). Channels of melted heat accumulating medium (2) through which the heat transfer medium can flow into further areas of the heat accumulating medium (2)can quickly form along the appendices (7), especially, if these are designed as good heat conductors.

A comparable effect is also present in the configuration which is represented in Fig. 3, at least, to the extent that the solid installations (8) provided protrude into both the heat transfer medium (3) and the heat accumulating medium (2). The fixed installations (8) are, for instance, held on the accumulator container via holding elements (9).

It is suggested that the fixed installations (8), preferably, are curved surfaces. Yet, a multitude of additional configurations of the curved surfaces is conceivable.

The characteristics of the invention which are disclosed in the above description, the drawings, and the Claims, can be of significance for the realization of the invention both individually and in any desirable combination. All of the disclosed characteristics are essential to the invention. The disclosed contents of the pertinent/attached priority documents (copy of pre-application) are hereby also fully incorporated in the disclosure of this application.

Patent Claims

1. Heat accumulating medium (2), such as paraffin, for a latent heat accumulator (1) (latent cold accumulator) which solidifies while forming crystal structures, characterized in that the crystal structures are modified by means of a structural additive, preferably,

in the sense of hollow structures, such as, for instance, hollow cones.

2. Heat accumulating medium in accordance or, specifically, in accordance with Claim 1, characterized in that the structural additive is homogeneously dissolved in the heat accumulating medium (2).

3. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that the structural additive belongs to the compound class of polyalkyl (meth)acrylates. /8

4. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that between 0.01 and 1 wt.% of the structural additive are added to the heat accumulating medium (2).

5. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that the heat accumulating medium (2) exhibits an (uncracked) oil component.

6. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that the oil constituent is between 0.1 and 10 wt.%.

7. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims,

characterized in that the heat accumulating medium (2) exhibits paraffinic hydrocarbons in a narrow cut.

8. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that the even-numbered, normal C chains (n-alkanes) are preferred.

9. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, whereas boiling structures (5) or nucleators (6) are contained, characterized in that the boiling structures or nucleators (6) exhibit such a specific weight that they, at least, float in the heat accumulating medium (2).

10. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that boiling structures (5)/nucleators (6) of various densities are contained.

11. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that boiling structures (5)/nucleators (6) are contained in a weight percentage of 1 to 10%.

12. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims,

characterized in that boiling structures (5)/nucleators (6) are glass structures, sandiver structures, plastic structures, or similar.

13. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that boiling structures (5)/nucleators (6) exhibit such a specific weight that they float partially in the heat transfer medium (3) and partially in the heat accumulating medium (2).

14. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that boiling structures (5)/nucleators (6) exhibit stalk-like appendices (7).

15. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that only the stalk-like appendices (7) protrude out of the heat accumulating medium (2) into the heat transfer medium (3).

16. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, /9
characterized in that an anti-foaming agent is, preferably, contained at a weight percentage of 0.01 to 5 wt.%.

17. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that the anti-foaming agent consists of a material on

the basis of silicones, polyalkoxylates, fatty alcohol alkoxylates, or carboxylic acid esters.

18. Heat accumulating medium in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that an antioxidant is, preferably, contained at a weight percentage of 0.001 to 0.1 wt.%.

19. Additive for a heat accumulating medium, such as paraffin, which solidifies while forming crystal structures, for a latent heat accumulator (latent cold accumulator), characterized in that a structural additive is contained which, preferably, modifies the crystal structures of the heat accumulating medium (2) in the sense of hollow structures, such as, for instance, hollow cones.

20. Additive in accordance with, or specifically in accordance with Claim 16, characterized in that the structural additive belongs to the compound class of the polyalkyl (meth)acrylates.

21. Additive in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that boiling structures (5) or nucleators (6) are contained which exhibit such a specific weight that they, at least, float in the heat carrier medium (2).

22. Additive in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that

boiling structures (5)/nucleators (6) of various densities are contained.

23. Additive in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that the boiling structures (5) or nucleators (6) are glass structures, sandiver structures, plastic structures, or similar.

24. Additive in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that an anti-foaming agent is contained.

25. Additive in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that the anti-foaming agent consists of a material on the basis of silicones, polyalkoxylates, fatty alcohol alkoxylates, or carboxylic acid esters silicone.

26. Additive in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that an antioxidant is contained.

27. Latent heat accumulator (or cold accumulator) with a heat accumulating medium in accordance with any of the Claims 1 to 18.

28. Latent heat accumulator in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that the boiling structures/nucleators are provided in the accumulator container as fixed installations (8).

29. Latent heat accumulator in accordance with, or specifically in accordance with one or several of the previous Claims, characterized in that the fixed installations (8) exhibit curved surfaces.

30. Use of a medium, such as paraffin, which solidifies while forming crystal structures, with an oil constituent as a heat accumulating medium for a latent accumulator.

31. Use in accordance with Claim 30, characterized in that the oil percentage is between 0.1 and 10 wt.%.

Accompanied by 3 page(s) of drawings.

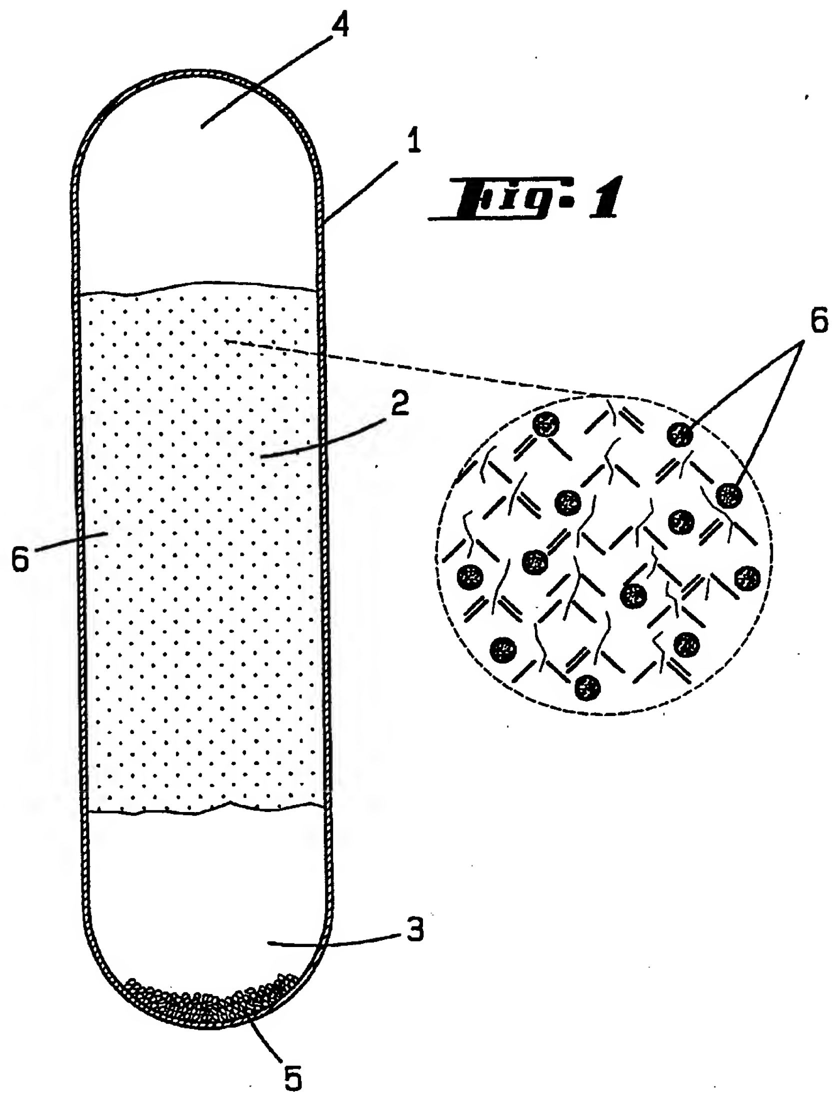

Fig. 1

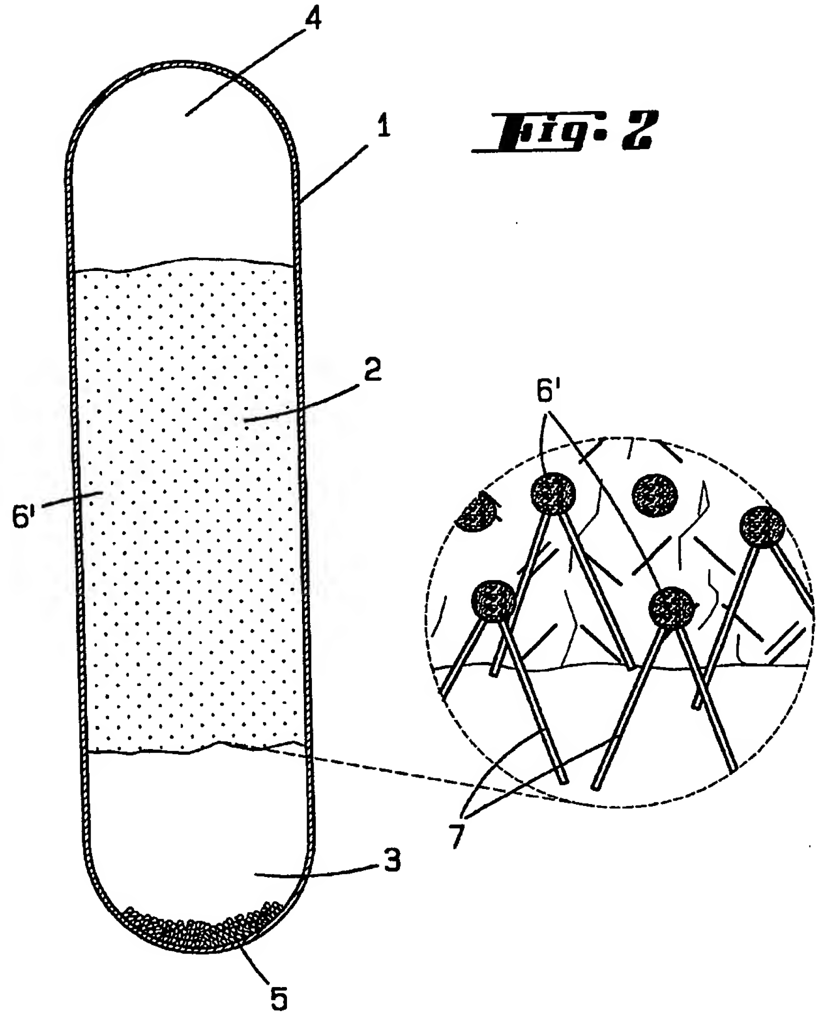

Fig. 2

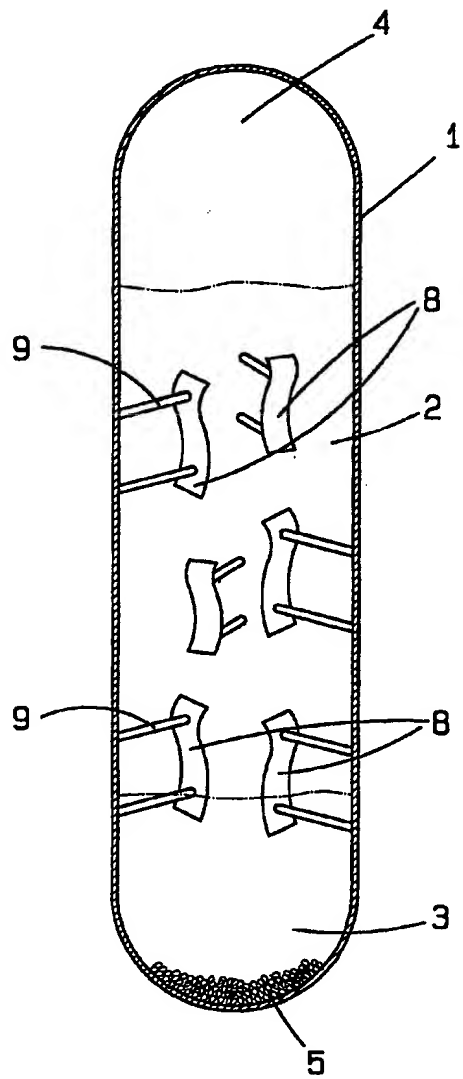

Fig. 3